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(54) Title: METHOD FOR THE PREPARATION OF A REINFORCED POLYMER COMPOSITION WHICH CONTAINS FIBRILS OF A CRYSTALLINE POLYOLEFIN

(57) Abstract

The invention relates to a method for the preparation of a reinforced polymer composition which contains fibrils of a crystalline polyolefin having a weight-average molecular weight (Mw) of at least 5×10^5 kg/kmol, particles of the crystallin polyolefin being converted into fibrils in a matrix material which is immiscible with the crystalline polyolefin, in which method the crystalline polyolefin has a maximum stretch ratio of at least 20 and the conversion to fibrils takes place at a t mperature below the melting point of the crystalline polyolefin. The invention also relates to reinforced polymer compositions obtainable by this method.

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METHOD FOR THE PREPARATION OF A REINFORCED
POLYMER COMPOSITION WHICH CONTAINS FIBRILS
OF A CRYSTALLINE POLYOLEFIN

The invention relates to a method for the
preparation of a reinforced polymer composition which
5   contains fibrils of a crystalline polyolefin having a
weight-average molecular weight (Mw) of at least
5×10^5 kg/kmol, particles of the crystalline polyolefin
being converted into fibrils in a matrix material which is
immiscible with the crystalline polyolefin.
10   A method of this type is disclosed in DE-A-2418803.
According to this "Offenlegungsschrift" a reinforced polymer
composition is obtained in which fibrils of the crystalline
high molecular weight polyolefin impart an increased
ultimate tensile strength to the polymer composition.
15   Preferably, the fibrils have a diameter of less than
5×10^{-5} m and a length of from 2×10^{-3} to 20×10^{-3} m. The
polymer composition has a homogeneous appearance on the
macroscopic scale. The polymer composition can be processed
to give films, sheets, tapes, sections and the like.
20   The temperature at which fibrils are formed in the
polymer composition lies in the region of the melting point
and preferably somewhat above the melting point of the
crystalline polyolefin. According to the examples for
polyethylene this temperature is approximately 150°C. If no
25   special measures are taken, relaxation occurs after the
formation of the fibrils and the fibrils can lose their
elongated shape. An example which is given of such a measure
is the cooling of the polymer composition under tension to a
temperature below the melting point of the crystalline
30   polyolefin. A disadvantage of this m asure is that it

demands accurate control of the processing conditions.
Moreover, some relaxation of the fibrils still always
5 occurs.

        The aim of the invention is, therefore, the
preparation of a polymer composition which is reinforced by
fibrils and has a high ultimate tensile strength, the
formation of fibrils taking place in an easily controllable
10 manner and relaxation of fibrils which have formed being
prevented.

        This aim is achieved in that, in the method
according to the invention, the crystalline polyolefin has a
maximum stretch ratio of at least 20 and the conversion to
15 fibrils takes place at a temperature below the melting point
of the crystalline polyolefin.

        Surprisingly, polymer compositions prepared
according to the invention have an appreciably higher
ultimate tensile strength and modulus of elasticity than th
20 known polymer compositions. The fibrils in the polymer
composition have an ultimate tensile strength (σ) of at
least 1 GPa and a modulus (E) of at least 20 GPa.

        Crystalline polyolefin having a maximum stretch
ratio of at least 20 is already known per se, for example
25 from US-A-4769433. This patent describes the stretching of
polyethylene of very high molecular weight which has never
been dissolved or melted ("virgin PE") and has been prepar d
by polymerisation at relatively low temperatures. This typ
of crystalline polyolefin with a high maximum stretch ratio
30. has a low entanglement density.

        The "virgin" polyethylene as prepared according to
US-A-4769433 can be further characterised by the difference
between the initial melting enthalpy of a sample and the
melting enthalpy which is obtained when the sample has been
35 completely melted and then solidified again. The difference
(fall) in melting enthalpies is preferably at least 10% of
the initial melting enthalpy and in particular at least 20%.
Moreover, the crystallinity of the polyethyl ne just
mentioned is high, at least 77% and pref rably more than

80%.
        Polyolefin having a high maximum stretch ratio can
5 also be obtained from polyolefin having a normal or low
   maximum stretch ratio via the so-called "gel route". In this
   procedure the polyolefin having a normal or low maximum
   stretch ratio is dissolved at elevated temperature in a
   suitable solvent, such as, for example, decalin, paraffin
10 oil or paraffin wax, the solvent being removed after
   cooling, for example by evaporation or extraction. The
   resulting material can be ground, preferably cryogenically,
   after which further processing can take place in the method
   according to the invention. polyolefin having a high maximum
15 stretch ratio, prepared in this way, does not always have to
   meet the crystallinity and melting enthalpy difference
   criteria given above.
        The maximum stretch ratio of the crystalline
   polyolefin is at least 20, preferably at least 40 and in
20 particular at least 80.
        The maximum stretch ratio is determined as follows:
   a layer of polyolefin powder 2 mm thick is compressed in a
   circular mould having a diameter of 5 cm for 5 minutes at
   room temperature under a weight of 50,000 kg. The circular
25 film obtained is then post-pressed at a temperature of 10°C
   below the melting temperature of the polyolefin (130°C for
   UHMWPE) for 10 minutes under a weight of 100,000 kg in a
   plane press. A dumbbell-shaped test piece with a length
   between the shoulders of 10 mm is punched from the film thus
30 obtained. This test piece is stretched in a Zwick 1445
   Tensile Tester at a temperature of 130°C, at a rate of
   10 mm/min until the test piece breaks. The maximum stretch
   ratio is determined as the quotient of the length of the
   section of the test piece between the shoulders when break
35 occurs in the test piece and the length of said section
   before stretching (10 mm).
        Melting temperatures Tm and melting enthalpies ΔH
   are determined by differential scanning calorimetry (DSC)
   using a scanning rate of 5°C/min and an initial t mperature

of 40°C. The DSC measurements were carried out, using a
Perkin Elmer DSC-7, on samples weighing 4×10^{-3} g.
5   Calibration of the DSC measurements was carried out using
Indium (Tm = 156°C and ΔH = 28.45 J/g). The melting enthalpy
ΔH is determined from the surface area beneath the melting
curve. Crystallinities (%) are calculated by dividing the
melting enthalpy ΔH of the sample by the melting enthalpy of
10   100% crystalline polymer. For polyethylene it is assumed
that the ΔH for 100% crystalline polymer is 293 kJ/kg.
        The weight-average molecular weight Mw is
determined using the methods known for this purpose, such as
gel permeation chromatography (GPC) and light scattering.
15   For polyethylene having a weight-average molecular weight Mw
of at least 5×10^{5} kg/kmol, Mw is calculated from the
intrinsic viscosity (IV), determined in decalin at 135°C.
The said weight-average molecular weights of 0.5 and
1.0×10^{6} kg/kmol correspond to an IV in decalin at 135°C of
20   5.1 and 8.5 dl/g respectively, in accordance with the
empirical relationship:
        $$M_{w} = 5.37 \times 10^{4} [IV]^{1.37}.$$
        Preferably, the weight-average molecular weight Mw
of the crystalline polyolefin is between 1×10^{6} and
25   10×10^{6} kg/kmol.
        According to the invention, crystalline
polyolefin is understood to be a homopolymer or copolymer of
an olefin, having a DSC crystallinity of at least 30%.
Preferably, the DSC crystallinity is at least 50%.
30   Examples of polyolefins to be used according to the
invention are polyethylene, polypropylene, polybutene and
poly-4-methylpentene-1.
        Advantageously very high molecular weight linear
polyethylene (ultra high molecular weight polyolefin or
35   UHMWPE) can be used in the method according to the
invention. UHMWPE is here understood to be linear
polyethylene having fewer than 10 side chains per 1,000
carbon atoms and preferably having fewer than 3 side chains
per 1,000 carbon atoms, or a poly thylene of this type which

also contains minor amounts, preferably less than 5 mol%, of
one or more other alkenes copolymerised ther with, such as
5   propylene, butene, pentene, hexene, 4-methylpentene, octene,
etc, which polyethylene or copolymer of ethylene has a
weight-average molecular weight of at least 5×10^5 kg/kmol.
The polyethylene can also contain minor amounts, preferably
at most 25% by weight of one or more other polymers, in
10 particular an alk-1-ene polymer, such as polypropylene,
polybutadiene or a copolymer of propylene with a minor
amount of ethylene.

Polyolefins that are used according to the
invention can, for example, be produced with the aid of a
15 Ziegler process or a Phillips process using suitable
catalysts and under known polymerisation conditions. See for
instance P. Blais and R. St.John Manley in Journal of
Polymer Science Part A-1, Vol. 6, 291-331 (1968).

The polyolefin can also contain non-polymeric
20 materials, such as solvents, waxes and fillers. The amount
of these materials can be up to 60% by volume relative to
the polyolefin.

The matrix material which is used according to the
invention and the crystalline polyolefin must be
25 thermodynamically immiscible under the conditions under
which the crystalline polymer is converted to fibrils. The
processing temperature of the matrix material must be below
the melting point of the crystalline polyolefin. Preferably
the matrix material is so chosen that the adhesion between
30 the matrix material and the crystalline polyolefin is good.
For this purpose, an adhesion improver can be added to the
matrix material and/or to the crystalline polyolefin.

The viscosity (η) of the matrix material is an
important parameter in the method according to the
35 invention. Depending on the conditions under which the
conversion of the crystalline polyolefin to fibrils takes
place, the viscosity must have at least a minimum value η_{min}
under th proc ssing conditions, which value is d termined
from the equation:

$$\eta_{min} = \tau_{min} / \gamma\cdot$$

in which τ_{min} is the minimum shear stress for conversion to
5   fibrils and $\gamma\cdot$ is the rate of shear. The minimum shear
stress τ_{min} depends on the crystalline polyolefin used.
For UHMWPE this is approximately $20-30 \times 10^{-4}$ N/m^2 at 120°C.
The rate of shear $\gamma\cdot$ depends on the equipment in which the
conversion to fibrils takes place and on the setting of this
10   equipment. The rates of shear to be achieved in various
equipment are known to those skilled in the art. The rate of
shear $\gamma\cdot$ is, inter alia, dependent on the geometry of said
equipment. In equipment in which high rates of shear occur,
the viscosity of the matrix material can therefore be lower
15   than in equipment in which the rates of shear remain low.

      The following may be mentioned as examples of the
matrix material: polyethylene, polypropylene, plasticised
polyvinyl chloride or copolymers based on these polymers and
rubbers; particularly suitable matrix materials are low
20   density polyolefin (LDPE), linear low density polyolefin
(LLDPE), very low density polyolefin (VLDPE), ethylene/vinyl
acetate copolymers, ethylene/propylene/(third monomer)
rubbers (EP(D)M rubbers) and styrene/butadiene rubber (SBR).

      Reactive substances, such as, for example,
25   vulcanising agents or 'crosslinking agents' can be
incorporated in the matrix material. These reactive
substances preferably have an activation temperature which
is above the processing temperature of the matrix material.
The activation temperature must, however, be below the
30   melting point of the crystalline polyolefin.

      The polymer compositions can be used in many
applications which are known for reinforced polymer
compositions, for example as construction material (mould
sections, sheets, sections, pipes or hoses) in laminates or
35   as films. Both rigid and flexible reinforced polymer
compositions can be obtained according to the invention. An
example of application of flexible reinforced polymer
composition is the application in a tyre for automobiles,
having increased puncture resistance.

A particular embodiment of the invention is that in
which, after forming of the fibrils, the matrix material is
5 separated from the fibrils. By selecting a suitable matrix
material, the fibrils can be separated herefrom, loose
fibrils of high tensile strength and rigidity being
obtained. The loose fibrils can be used in various
applications, as staple fibres. The separation of matrix
10 material and fibrils can be carried out, for example, by
dissolving or melting the matrix material.

According to the invention, fibrils is used to
denote bodies having a length (L) which is large compared
with the width and the thickness or the diameter (D). For a
15 fibril, the L/D ratio is at least 4, preferably at least 10
and in particular at least 25. Fibrils of varying diameter
and length are present in a polymer composition prepared
according to the invention. Usually the dimensions of the
fibrils are such that the said fibrils have a diameter of
20 less than 5×10^{-4} m and a length of 2×10^{-3} to 100×10^{-3}
m. Preferably, the fibrils have a diameter of less than $3 \times$
10^{-4} m, in particular less than 1×10^{-4} m. The particle
size of the crystalline polyolefin from which the fibrils
are prepared is of importance for the dimensions of the
25 fibrils.

The temperature T_σ, at which the crystalline
polyolefin is converted into fibrils, must be higher than
the processing temperature of the matrix material but lower
than the melting point of the crystalline polyolefin.
30 The mixing of the crystalline polyolefin and
the matrix material and the conversion to fibrils can take
place in equipment suitable for applying shear stresses and
for generating extensional flow. Preferably, high tensile
stresses can be applied in this equipment to the polymer
35 composition located in the equipment. Examples of such
equipment are extruders and injection moulding machines,
provided with conically tap red screw sections and/or
Couette sections, rollers, and Brabender mix rs.

Depending on the conditions during the formation of

th fibrils, it is possible, with th aid of the m thod according to the invention, to prepare anisotropic polymer
5 compositions which are oriented in a specific direction and consequently have a higher ultimate tensile strength and modulus in this direction than in other directions.

The invention is illustrated below with reference to the following illustrative embodiments.
10

Example I

The matrix material used is an ethylene/vinyl acetate copolymer (EVA) which has a melt index (determined in accordance with ASTM standard D1238 at 190°C and with a
15 load of 2.16 kg) of 0.2, of the ELVAX 670 type from Du Pont. Crystalline high molecular weight polyethylene (polyolefin) is prepared in accordance with Example 5 of US-A-4769433. The crystalline polyethylene thus obtained has an intrinsic viscosity (I.V.) of 30 and a molecular weight
20 (M_w) of 5.6 x 10^6. The melting point is 142°C. The average particle size of the crystalline polyethylene particles is 900 μm. The maximum stretch ratio of the polyethylene is 100. With the aid of a roller of the Collin 150 x 450 type (Walzwerk Dr Collin GmbH), a polymer composition is prepared
25 from 90 g of matrix material and 10 g of crystalline polyolefin.

Rolling procedure:

The matrix material is processed on the roller
30 at a rolling temperature of 110°C until a rolled sheet is formed. The speed of rotation of the two rolls of the roller is 10 revolutions per minute (no friction, RPM=10). After 2 minutes, the crystalline polyolefin is uniformly sprinkled over the rolled sheet. After waiting for 1 minute, the speed
35 of revolution of one of the rolls of the roller is increased to RPM=20. The gap between the rolls is adjusted to 0.1 mm. After rolling for 3 minutes, the roller is stopped and the polymer composition form d is removed from the roller.

Pressing:

22 g of the polymer composition formed after th

5   rolling procedure are pre-pressed at a temperature of 90°C
and under a weight of 1,000 kg for 30 s in a mould for eight
150 x 50 x 3.2 mm plates. The amount (22 g) is calculated
from the total volume of the mould and the density of the
polymer composition, a 5% excess being maintained. The

10 polymer composition is then pressed at a temperature of
120°C and under a weight of 50,000 kg for 7 minutes in the
steel mould to a thickness of 3.2 mm, after which the shap d
polymer composition is cooled at a rate of 40°C/minutes.

The determination of the ultimate tensile strength

15 (σ), the modulus (E) and the elongation at break (ε) of the
polymer composition is carried out in accordance with ISO
standard 37 type 2 on a test rod having a thickness of
3.2 mm, at a pulling speed of 20×10^{-3} m/minute.

A fibre approximately 40 mm long is taken from the

20 polymer composition and the tensile strength of said fibre
is determined with the aid of a Zwick 1445 type tensile
testing machine. A fibre 40 mm long is clamped in the clamp
of the tensile testing machine over a clamping length (gauge
length) of 20 mm. The pulling speed is adjusted to 0.5 times

25 the clamping length per minute. The cross-section of the
fibre is calculated from measured values for the length and
the density of the fibre. The characteristics of the polymer
composition are given in Table 1.

If the matrix material is processed as described

30 above without crystalline polyolefin, a material is obtained
which has an ultimate tensile strength σ of 20 MPa, a
modulus E of 52 MPa and an elongation at break ε of 928%.

Example II

35 A polymer composition is prepared as in Example I
but in this case from 80 g of matrix material and 20 g of
crystalline polyolefin. The results are given in Table 1.

Example III

A polymer composition is prepared as in Example I
5 but in this case from 70 g of matrix material and 30 g of
crystalline polyolefin. The results are given in Table 1.

Example IV

A polymer composition is prepared as in Example I
10 but in this case from 60 g of matrix material and 40 g of
crystalline polyolefin. The results are given in Table 1.

Table 1

Results of Examples I-IV: influence of the amount
15 of UHMWPE (matrix material is EVA, rolling temperature
110°C)

Example	Amount of UHMWPE (% by wt.)	Fibril formation	Fibrils σ (GPa)	E (GPa)	Polymer composition σ (MPa)	E (MPa)	ε (%)
I	10	yes	1.8	31	10	80	140
II	20	yes	1.0	21	12	132	47
III	30	yes	1.5	31	12	130	39
IV	40	yes	1.3	20	17	184	27

Examples V, VI and comparative Examples A and B

In Examples V and VI and comparative Examples A and
B the influence of the processing temperature on the
30 properties of the polymer composition obtained is
investigated. A polymer composition is prepared as in
Example I but in this case from 80 g of matrix material and
20 g of crystalline polyolefin. The rolling temperature is
varied from 120-150°C for the various examples. The results
35 are given in Table 2.

It is seen from this series of examples that if
highly stretchable UHMWPE is processed above its melting
point no fibril formation occurs.

Table 2

         Results of Examples V and VI and comparative

5   Examples A and B: influence of rolling temperature (matrix material is EVA; amount of UHMWPE 20% by weight).

Example	T_{roller}	Fibril formation	Fibrils		Polymer composition		
	(°C)		σ (GPa)	E (GPa)	σ (MPa)	E (MPa)	ε (%)
V	120	yes	1.9	23	11	153	54
VI	130	yes	1.7	26	12	165	54
A	140	no	–	–	7	60	129
B	150	no	–	–	7	62	74

       In comparative Examples C to G inclusive the influence of the type of crystalline polyolefin on the

20   properties of the polymer composition obtained is investigated. It is found that if UHMWPE which has a maximum stretch ratio of less than 20 is used, no fibril formation takes place below the melting point and above the melting point (Example G) relaxation of the fibrils formed occurs,

25   as a result of which ultimately no fibrils are present in the polymer composition.

Comparative Example C

       A polymer composition is prepared as in Example I,

30   but using, as the starting materials, 80 g of ethylene/vinyl acetate of the type Elvax[r] 670 as matrix material and 20 g of crystalline polyethylene of the type Stamylan UH510 from DSM. This crystalline polyethylene has a maximum stretch ratio of 1. The melting point is 140°C. The roller

35   temperature is 120°C. The results are given in Table 3.

Comparative Example D

       A polymer composition is prepared as in Example I but using, as the starting materials, 80 g of ethylene/vinyl

acetate of the type Elvax[r] 670 as matrix material and 20 g
of crystalline polyethylene of the type HIFAX 1900[r] from
5 Hercules. This crystalline polyolefin has a maximum stretch
ratio of 16. The melting point is 142°C. The roller
temperature is 120°C. The results are given in Table 3.

Comparative Example E
10   A polymer composition is prepared as in Example D
but 20 percent by weight of decalin, calculated relative to
the crystalline polyethylene, is added to the crystalline
polyethylene of the type HIFAX 1900[r]. The roller temperatur
is 120°C. The results are given in Table 3.
15

Comparative Example F
          A polymer composition is prepared as in Example E,
but the roller temperature is 130°C. The results are given
in Table 3.
20

Comparative Example G
          A polymer composition is prepared as in Example I
but using, as the starting materials, 80 g of ethylene/vinyl
acetate of the type Elvax[r] 670 as matrix material and 20 g
25 of crystalline polyethylene of the type Stamylan UH210 from
DSM. This crystalline polyolefin has a maximum stretch ratio
of 1. The melting point is 142°C. The roller temperature is
150°C. The results are given in Table 3.

Table 3

         Results of comparative Examples C-G: influence of type of UHMWPE. (* = containing 20% by weight of decalin)

Example	Type of UHMWPE	T_{roller} (°C)	Fibril formation	Polymer composition		
				σ (MPa)	E (MPa)	ε (%)
C	UH510	120	no	7.4	64	575
D	HIFAX1900	120	no	6.5	64	414
E	HIFAX1900*	120	no	6.6	54	369
F	HIFAX1900*	130	no	7.7	57	424
G	UH210	150	no	9.5	54	483

Examples VII-IX

         In Examples VII to IX inclusive, LDPE having a density of 0.921 kg/m^3, of the type Stamylan 2101 TN04 from DSM, is used as matrix material. A polymer composition is prepared as in Example I, but using, as the starting materials, 80 g of LDPE as matrix material and 20 g of crystalline polyolefin of the type from Example I. In Examples VII to IX inclusive, the roller temperature is varied. The results are given in Table 4.

         If the LDPE matrix material is processed as described above without crystalline polyolefin, a material is obtained which has an ultimate tensile strength (σ) of 12 MPa, a modulus (E) of 121 MPa and an elongation at break (ε) of 915%.

Table 4

Results of Examples VII-IX: influence of the roller
temperature (matrix material = LDPE; 20% by weight of
UHMWPE)

Example	T_{roller}	Fibril formation	Fibrils		Polymer composition		
			σ	E	σ	E	ε
	(°C)		(GPa)	(GPa)	(MPa)	(MPa)	(%)
VII	130	yes	0.7	13	10.2	252	31
VIII	120	yes	1.2	25	19.6	335	27
IX	110	yes	1.2	24	7.9	94	92

Examples X and XI and comparative Examples H, J and
K relate to mixtures in which the matrix material is a
rubber. The results are given in Table 5.

Example X

(A) Using a simultaneously rotating twin-screw
extruder, a suspension of 15% by weight of UHMWPE of the
type HB 312 from Himont, having a weight-average molecular
weight of 1.5×10^6 kg/kmol is converted to a homogeneous
solution in decalin at about 180°C. The solution is extruded
as a plane sheet having a thickness of 1.0 mm and cooled
until a gel forms. After evaporating the decalin, the sheet
formed is ground to a fine powder having an average particle
size of 900 μm. The crystalline polyolefin powder obtained
has a maximum stretch ratio of 43.

(B) 10% by weight of the powder obtained in the
above manner is added to an ethylene/propylene/diene rubber
(EPDM) compound of the type Keltan 512 x 50 from DSM. Using
this compound, a mixture is prepared in accordance with ISO
4097-1980(E), which mixture is then rolled for 5 minutes at
120°C using the rolling procedure as described in Example I,
UHMWPE fibres being formed. After rolling, one part by
weight of vulcanising agent of the type Rhenocure AT from

Rheinau GmbH is mixed rapidly with 272 parts by weight of
the compound, after which the latter is vulcanised for 30
5   minutes at 120°C.

Example XI
         A compound which contains 20% by weight UHMWPE in
EPDM is prepared as in Example X.
10

Comparative Example H
         A compound is prepared as in Example X under (B),
using UHMWPE of the type HB 312 from Himont directly as the
starting material, without pre-processing via a solution.
15   The UHMWPE has a maximum stretch ratio of 1.

Comparative Example J
         A compound is prepared as in Example X, except that
vulcanisation takes place at 160°C.
20

Comparative Example K
         A compound is prepared as in Example X under (B),
but without UHMWPE.

25   Table 5
         Results of Examples X and XI and comparative
Examples H, J and K (matrix material is
ethylene/propylene/diene rubber):

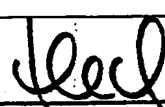| 30 Example	Via solution	Amount of UHMWPE ($\%$ by wt)	Vulcanisation temperature ($°C$)	Polymer composition	
				σ (MPa)	E (MPa)
X	yes	10	120	78	5.4
35 XI	yes	20	120	95	7.2
H	no	10	120	45	3.1
J	yes	10	160	50	7.8
K	—	0	120	42	1.9

It follows from the results that polyethylene
processed via solution, which has a maximum stretch ratio of
5   43, gives a great improvement in the ultimate t nsile
strength and modulus of elasticity. If the polymer
composition is vulcanised at a temperature of 160°C, that is
to say above the melting point of the polyolefin, the
ultimate tensile strength remains much lower.

C L A I M S

5   1.   Method for the preparation of a reinforced polymer
          composition which contains fibrils of a crystalline
          polyolefin having a weight-average molecular weight Mw
          of at least 5×10^5 kg/kmol, particles of the
          crystalline polyolefin being converted into fibrils in a
10   matrix material which is immiscible with the crystalline
          polyolefin, characterised in that the crystalline
          polyolefin has a maximum stretch ratio of at least 20
          and the conversion to fibrils takes place at a
          temperature below the melting point of the crystalline
15   polyolefin.
     2.   Method according to Claim 1, characterised in that the
          crystalline polyolefin has a weight-average molecular
          weight Mw of 1×10^6 to 10×10^6 kg/kmol.
     3.   Method according to Claim 1 or 2, characterised in that
20   the crystalline polyolefin is polyethylene, having a
          maximum stretch ratio of at least 40.
     4.   Method according to Claim 3, characterised in that the
          crystalline polyolefin has a maximum stretch ratio of at
          least 80.
25   5.   Method according to Claims 3 or 4, characterised in that
          the crystalline polyethylene has a DSC melting point of
          at least 140°C.
     6.   Method according to one of Claims 1-5, characterised in
          that the crystalline polyolefin has a crystallinity of
30   at least 80%.
     7.   Method according to one of Claims 1-6, characterised in
          that the matrix material consists of a thermoplastic
          rubber.
     8.   Method according to one of Claims 1-6, characterised in
35   that the matrix material consists of a low density
          polyolefin (LDPE).
     9.   Reinforced polymer composition obtainable using the
          method according to one of Claims 1-8.
     10. Fibrils obtainable using the method according to one of
40   Claims 1-8, after separating off the matrix material.

INTERNATIONAL SEARCH REPORT

International Application No PCT/NL 91/00061

I. CLASSIFICATION F SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[5]: C 08 J 5/04; D 01 F 8/06; C 08 J 5/18

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC[5]	D 01 F, C 08 J

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [*]	Citation of Document, [11] with Indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
Y	EP, A, 0106764, (SOCIETE CHIMIQUE DES CHARBONNAGES) 25th April 1984 see the claims.	1-9
Y	US, A, 4123476 (A. BONNEFON et al.) 31st October 1978, see claims & DE, A, 2418803 cited in the application	1-9
A	EP, A, 0043288 (BXL PLASTICS LTD) 06th January 1982	
A	FR, A, 2387115 (UBE INDUSTRIES LTD.) 10th November 1978 see claims	1
A	EP, A, 0260974 (THE DOW CHEMICAL COMPANY) 23rd March 1988 ./.	

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
10th July 1991	1 6. 09. 91

International Searching Authority	Signature of Authorized Officer
EUROPEAN PATENT OFFICE	Falk Heck

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, " with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	US, A, 3546063 (A.L. BREEN) 08th December 1970 see claims; column 7, lines 46-49	10
A	EP, 0322838 (TEIJIN LIMITED) 05th July 1989	

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 30/08/91
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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